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AN IMPROVED CONTINUOUS ETHER EXTRACTOR FOR THE DETERMINATION OF URANIUM IN DISSOLVER SOLUTIONS

by

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ABSTRACT

An improved continuous ether extractor is described. The modifications include a means of safely disposing of the active raffinate and a means of positively checking the raffinate for completeness of uranium extraction. The results obtained on synthetic samples and on dissolver solutions are given.

This work was undertaken because of a need for the determination of uranium in dissolver solutions with an accuracy of 0.1 per cent. After a review of available methods it was decided that a gravimetric determination would meet the requirements of precision and accuracy. However, owing to the high level of beta and gamma activity ranging from a few hundred mr to several r per hour per ml, it was necessary to make a prior separation of the uranium. Of the solvent extraction procedures available, ether extraction appeared to be most advantageous. The purpose of this paper is to describe an improved continuous ether extractor and its use in the quantitative determination of uranium.

The apparatus, shown in Figure 1, permits the introduction of the sample and removal of the extracted solution without disassembly. It also provides for mixing and for a method of obtaining a sample of the extracted solution which can be tested for completeness of extraction, if it is so desired. Since only about five minutes need be spent near the apparatus during an extraction, the shielding requirements are reduced. In fact, no shielding was used other than that provided by a Blickman hood in which the entire apparatus was contained. The amount of β, γ activity coming through the hood window never exceeded 20 mr/hr. The uranium is extracted quantitatively and decontaminated to the extent that an ordinary gravimetric uranium determination with NH_4OH can be performed without a radiation hazard to the analyst. Although the apparatus can be built to any convenient size, it is important that the top of the drain tube, D, be higher than the point of ether overflow, so that if the air pressure were inadvertently shut off, the sample solution would not overflow into I and be lost. Also the point at which the sample solution enters into the extractor, C, is critical. If higher than shown, the possibility always exists that sample solution will flow around the inside of the extractor and go directly into flask A. If lower than shown, the sample solution will rise into tube G and may not be completely extracted.

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FIGURE 1
SCHEMATIC DIAGRAM OF URANIUM
EXTRACTION APPARATUS.

LEGEND

- A 500-ml flat-bottomed Florence flask with $\frac{1}{4}$ 24/40 female joint.
- B Four-inch variable temperature control hot plate.
- C Extractor.
- D Drain tube. Made from 7 mm o. d., 1 mm i. d. capillary tubing.
- E Ether dispersing tube. Made from 7-mm tubing with coarse sintered glass filter. Receiving end fitted to tip of condenser to receive ether condensate and fluted to rest on indented part of extractor at three points so as to allow the passage of ether vapor.
- F Friedrichs condenser; 35 cm length.
- G Sample entrance tube. Volume ca. 10 ml with 1-hole 2-mm stopcock and attached with 8-mm tubing.
- H Two-way stopcock; 2-mm bore.
- I Raffinate aliquot tube. The inner tube is adjusted to a length such that when raffinate is sucked out of extractor and stopcock H vented to the air, ca. 1 ml of raffinate remains in the tube I, thus taking a 1/20 aliquot of the raffinate solution.
- J Two-way stopcock; 2-mm bore.
- K Mechanical pump. Vented in hood.
- L Safety bottle. Made from two-liter suction flask.
- M Nine-liter shielded liquid active waste container.

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To operate this apparatus, a 0.752-ml aliquot of the sample solution is introduced via tube G. The pipette is rinsed three times with saturated NH_4NO_3 solution into the extractor, C. Tube G is finally washed down with saturated NH_4NO_3 solution until the volume in the extractor, C, is 10 to 15 ml. A very small positive air pressure is maintained in tube D. This serves to prevent the sample solution from entering the drain tube, D, during extraction and provides additional stirring. In practice the globules of ether rising through the solution produce adequate mixing. Normally the air flow is kept to a minimum. The receiving flask, A, containing 75 ml of water and 75 ml of ether is supported by a small hot plate, B, adjusted so that the rate of distillation of ether during the extraction is ca. 8 ml per minute. The sample is extracted for one hour with the addition, at 15-minute intervals, of one to two ml of concentrated HNO_3 saturated with NH_4NO_3 , the first addition being made 15 minutes after the extraction began. After the third addition of acid, saturated NH_4NO_3 is added to bring the ether- NH_4NO_3 interface almost to the point of the ether overflow, thus making the volume of the aqueous phase in the extractor, C, ca. 20 ml. At the end of the extraction, the receiving flask, A, is detached from the apparatus, heated for a few minutes to boil off the ether, and then set aside for uranium determination as described below.

The raffinate is then removed from the apparatus by connecting the pump, K, to the extractor, C, by means of stopcock J so that the raffinate is sucked into the shielded liquid active waste container, M. The solution is sucked from the extractor, C, until the NH_4NO_3 -ether interface just reaches the bottom of the extractor, C. This is accomplished by venting stopcock H to the air at the appropriate moment. The reason for venting at this time is to prevent appreciable amounts of ether from being sucked into the shielded container, M, and possibly causing undesirable side reactions within the container. Also, if any ether was collected in tube I, a representative sample of the raffinate would be obtained. After turning stopcocks H and J so that air is again flowing through the extractor, C, tube I containing ca. 1 ml of the raffinate is detached from the line, and the contents are transferred to a 15-ml stoppered centrifuge tube for uranium analysis as described below. After tube I is rinsed out and replaced on the line, the apparatus is ready to receive another sample.

Although only the use of the apparatus for the separation of uranium from dissolver solutions is considered in this paper, it is obvious that, with simple modification, a quantitative recovery of the raffinate is possible. This can be done if one substitutes a suitably sized flask with appropriately sized standard female joint for tube I and transfers the raffinate into the flask along with washings of the extractor. An example where such a technique would be useful is the separation of zirconium from uranium followed by the determination of each element in the separated phases.

The uranium determination is made as follows: The extracted uranium solution is quantitatively transferred from the receiving flask, A, to

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a 250-ml beaker. Twenty ml of 45 per cent NH_4NO_3 solution is added, the solution is heated to near boiling, and the uranium is precipitated by the addition of 10 ml ca. 14N NH_4OH (prepared by saturating H_2O with NH_3 and storing in a polyethylene bottle). The ammonium diuranate precipitate is allowed to settle for a few minutes and then filtered through a Whatman 42 paper using a dilute NH_4NO_3 solution (2%) which has been neutralized with NH_4OH as a wash solution. The paper is then burned off, and the precipitate is ignited to constant weight at 825 to 850°C and weighed as U_3O_8 . The precipitation, filtration, ignition, and weighing operations are performed in a hood since the extract is still appreciably radioactive.

The one-ml aliquot of the raffinate is analyzed spectrographically for uranium to verify complete extraction. It is necessary to destroy the NH_4NO_3 in the solution since it interferes with the spectrographic determination of the uranium. This is done using a wet oxidation procedure as follows.

The one ml of raffinate solution contained in the 15-ml centrifuge tube is diluted to ca. 8 ml with water, and five drops concentrated HNO_3 plus 10 drops concentrated HCl are added. The solution is heated in a water bath for about one-half hour. Then one ml HNO_3 plus one ml HCl are added, and the solution is evaporated to dryness by blowing a stream of air on the solution while heating on the water bath. The addition of acid and evaporation to dryness is repeated until no salts are visible upon evaporation to dryness. One ml concentrated HCl is added, and the solution is submitted for spectrographic determination by the copper spark method.¹ The spectrographic laboratory reported the uranium as less than 200 micrograms in the total raffinate of every sample tested. Obviously any alternative procedure sensitive enough for detecting uranium in the raffinate could be used if convenient.

The results obtained on solutions of known uranium content are shown in Table I. These data are the values obtained on aliquots of a pure uranyl nitrate solution prepared from primary standard grade (MSST) U_3O_8 . The average of four determinations gives a value differing from the standard value by 0.1 per cent. The standard deviation of a single determination is 0.17 mg or 0.1 per cent.

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¹ M. Fred, N. H. Nachtrieb, and F. S. Tomkins, J. Opt. Soc. Am. 37, 279 (1947).

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Table I
RESULTS ON KNOWN URANIUM SOLUTIONS

Solution Number	Solution Contains (mg U_3O_8 /ml)	Uranium Found (mg U_3O_8 /ml)
1	0.01870	0.01874
2	0.01870	0.01872
3	0.01870	0.01873
4	0.01870	0.01870
Average		0.01872 ₃

Most of the data obtained are based upon the volume of a 750 λ pipette which was used to take the aliquots of the samples and synthetic solutions. This pipette was calibrated by gravimetrically determining the uranium content of aliquots of a standard uranium solution. The actual volume obtained by calibration was 752 λ . The average deviation on three calibration determinations was one part per thousand. The accuracy of the calibration was estimated to be 0.15 per cent.

CONCLUSION

A continuous ether extractor has been described which has proved to be particularly adaptable for the quantitative separation of uranium from radioactive solutions. The principle advantages of the apparatus are the ease with which highly radioactive raffinates can be disposed of via the built-in drain tube, the ability to ascertain the completeness of uranium extraction, the ability to quantitatively obtain the raffinate if desired, and the little time that need be spent close to the extractor during a run. Although a large degree of decontamination is achieved, the extracted uranium still contains appreciable amounts of radioactivity. Therefore it is necessary to observe the usual precautions during the final steps of the determination. Data have been presented to indicate the accuracy and precision obtained.